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(74) Agent: SYNGENTA PARTICIPATIONS AG; Intellectual Property, P.O. Box, CH-4002 Basel (CH).

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(71) Applicant (*for all designated States except US*): SYNGENTA PARTICIPATIONS AG [CH/CH]; Schwarzwaldallee 215, CH-4058 Basel (CH).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): CHOW, Victor, Shui-Chiu [US/US]; 4622 Chesterfield Place, Jamestown, NC 27282 (US). MERRITT, Douthitt, Pruitt [US/US]; 2208 Rheims Drive, Greensboro, NC 27407 (US). HAULSEE, Lear, Michael [US/US]; 2278 Chimney Swift Circle, Marietta, GA 30062 (US).

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(54) Title: PESTICIDE FORMULATIONS CONTAINING PHOSPHATE ESTER SURFACTANT AND ALKOXYLATED LIGNOSULFONATE

(57) Abstract: The present invention relates to a surfactant system for general use in agricultural compositions, including, but not limited to herbicidal, fungicidal and insecticidal formulations comprised of two components: an alkoxyated polyarylphenol phosphate ester surfactant in combination with an alkoxyated lignosulfonate salt surfactant.



**WO 01/20986 A1**

**PESTICIDE FORMULATIONS CONTAINING PHOSPHATE ESTER SURFACTANT AND ALKOXYLATED  
LIGNOSULFONATE**

**FIELD OF THE INVENTION**

The present invention relates to a surfactant system for general use in agricultural compositions, including, but not limited to herbicidal, fungicidal and insecticidal formulations comprised of two components: an alkoxyated polyarylphenol phosphate ester surfactant in combination with an alkoxyated lignosulfonate salt surfactant.

**BACKGROUND OF THE INVENTION**

Alkylphenol ethoxylates (APE's) and their anionic derivatives are surfactants that are well known to industry and have historically been relied upon heavily by agricultural chemical producers. However, formulations containing APEs do not always provide the most desirable combination of design specifications, e.g. product efficacy, working parameters and cost. Traditional non-APE surfactant systems have not been readily adaptable substitutes for APE surfactants. For example, depending on the formulation requirements, calcium dodecylbenzenesulfonate used in conjunction with fatty acid ethoxylates has proven to be an unacceptable APE substitute because of poor performance within one or more design parameters such as emulsion stability, acute toxicity, temporal and thermal stability, chemical and physical stability; solution, suspension or dilution dynamics, and viscosity and suspension stabilization. The inability of industry to adapt existing technology to improve upon characteristics of surfactant systems containing APEs has prompted the development of entirely new line APE surfactants. The additional challenge faced by the scientific community has been to develop new APE surfactants which can be easily made from readily available and cost effective raw materials. Accordingly, there continues to be a need for improved APE surfactants.

**SUMMARY OF THE INVENTION**

Surprisingly, it has now been discovered that the combination of alkoxyated polyarylphenol phosphate esters (or salts or acid forms thereof) with alkoxyated lignosulfonate salts provides a suitable surfactant system for general use in agricultural

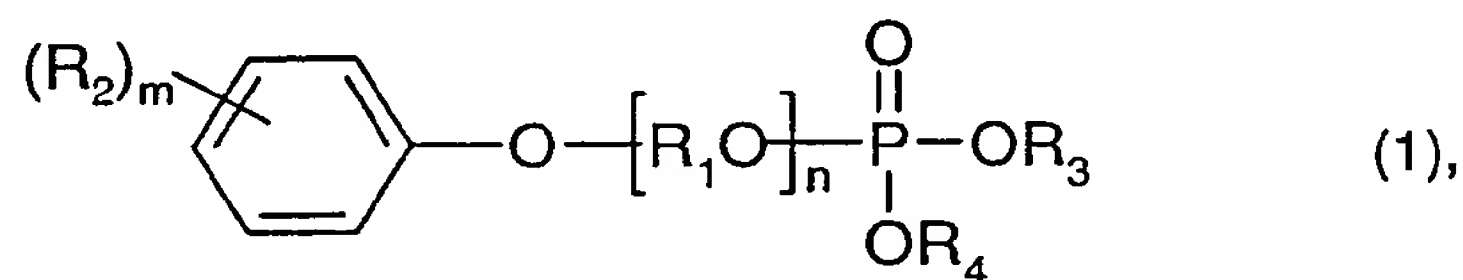
products. The surfactant system of the instant invention has been found to provide superior performance in aqueous suspension concentrates of pesticides. The instant invention includes the surfactant composition comprising one or more alkoxyated polyarylphenol phosphate esters (or salts or acid forms thereof) and one or more alkoxyated lignosulfonate salts. The invention also includes the agrochemical formulations containing the instantly disclosed surfactant system. In one embodiment of the invention, the compositions containing the instant surfactant system do not contain or are substantially free of other known APEs. The surfactants of the instant invention are obtained from combining the appropriate alkoxyated polyarylphenol phosphate ester with the appropriate alkoxyated lignosulfonate salt.

The steric configuration of the polyarylphenol group additionally seems to protect the appropriate alkoxyated polyarylphenol phosphate ester surfactant component of the surfactant system from hydrolytic cleavage typically observed in other known anionic phosphate based surfactant systems.

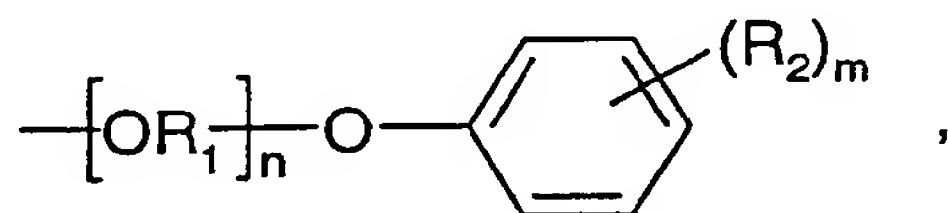
### DETAILED DESCRIPTION OF THE INVENTION

One aspect of the invention is the surfactant system comprising:

a) at least one alkoxyated polyarylphenol phosphate ester of the formula (1):



wherein  $R_1$  independently is a straight chain or branched  $C_2$ - $C_4$  alkylene,  $R_2$  is phenyl, aryl or alkylaryl, wherein the phenyl nucleus in  $R_2$  is unsubstituted or substituted by one to three groups selected from the group consisting of  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  alkoxy, and  $R_3$  and  $R_4$  are independently selected from the group consisting of hydrogen, sodium, potassium, and

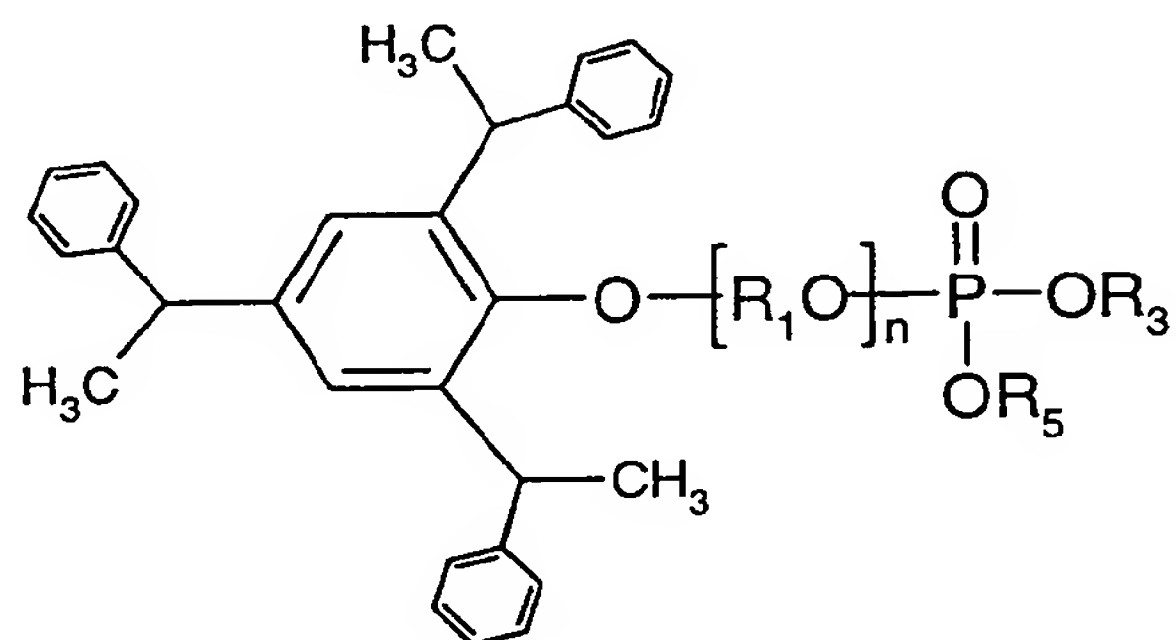


$m$ , is 2 or 3, and  $n$  is a number from 1 to 150 inclusive, and

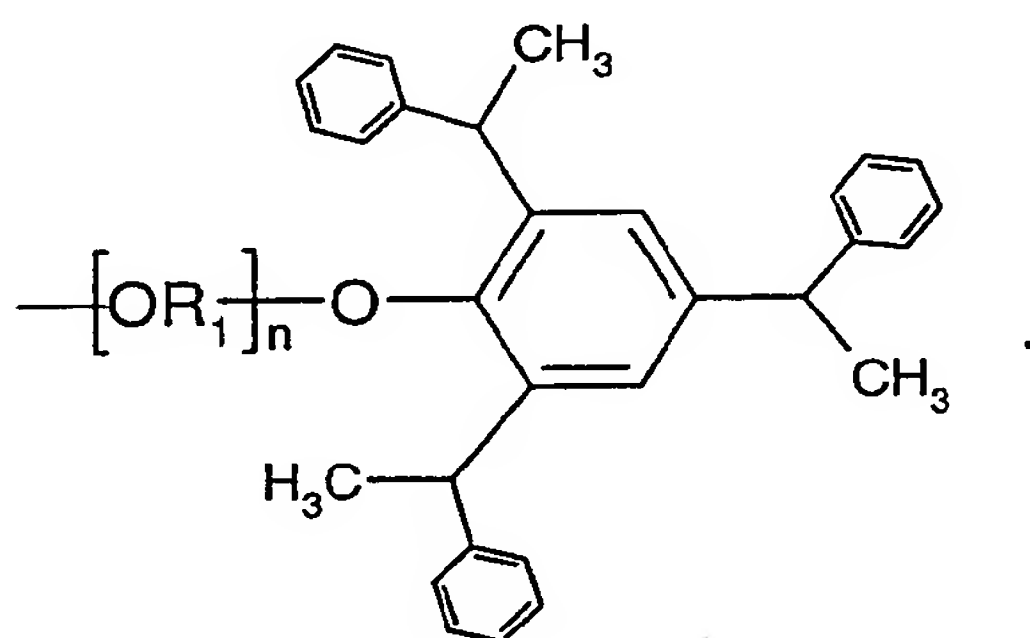
b) at least one alkoxyated lignosulfonate salt.

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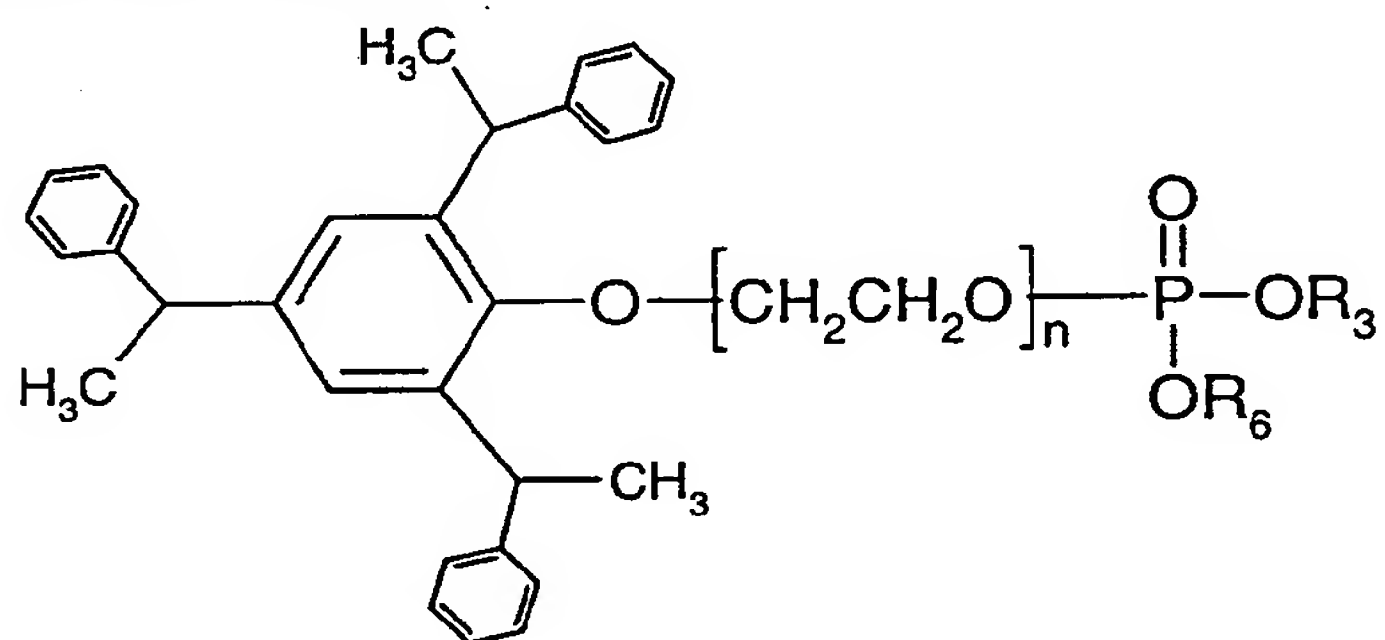
A more preferred embodiment of the invention is the surfactant system, wherein component (a) is the phosphate ester having the formula:



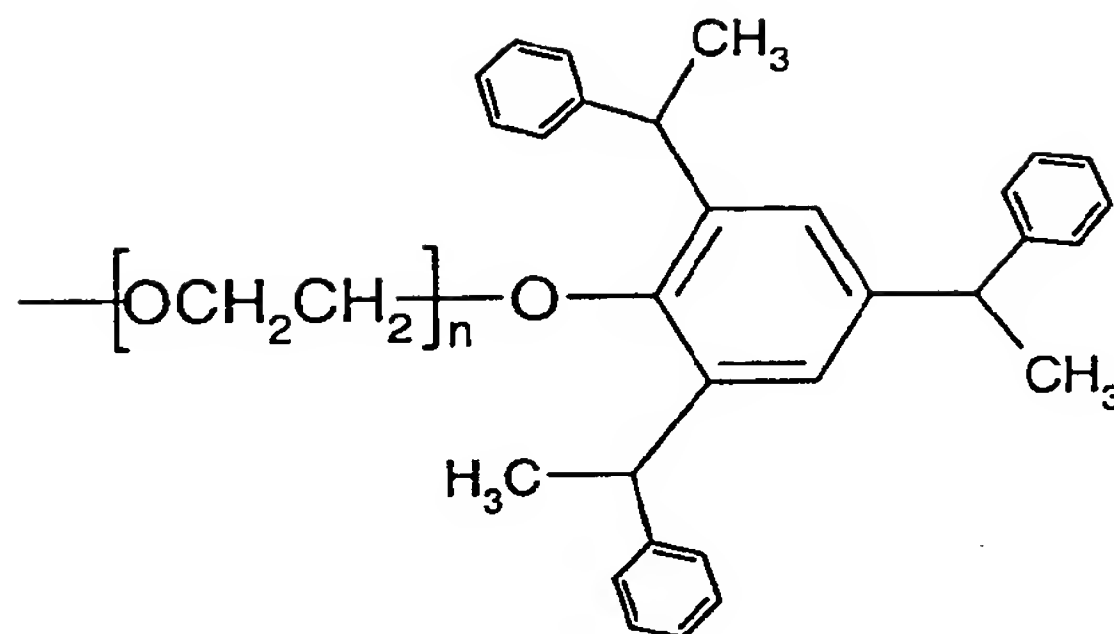
wherein  $R_1$  and  $n$  are defined as above, and  $R_3$  and  $R_5$  are independently selected from the group consisting of hydrogen, sodium, potassium, and



The invention also includes the surfactant system, wherein component (a) is the phosphate ester having the formula:



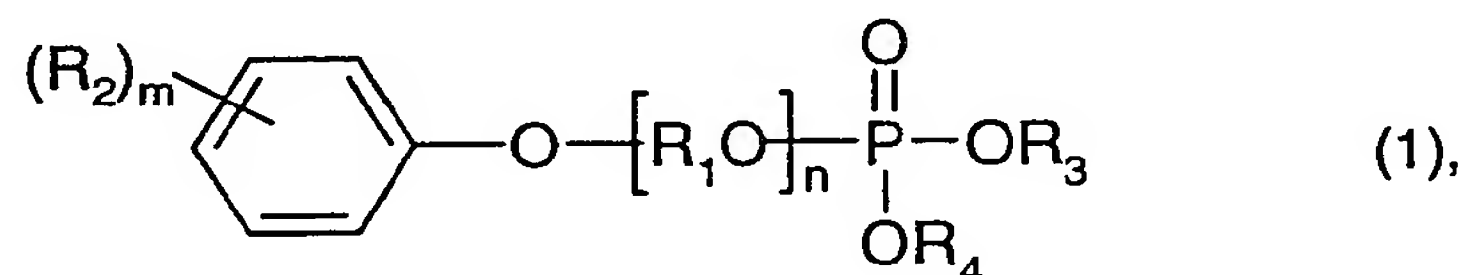
wherein  $n$  is defined as above, and  $R_3$  and  $R_6$  are independently selected from the group consisting of hydrogen, sodium, potassium, and



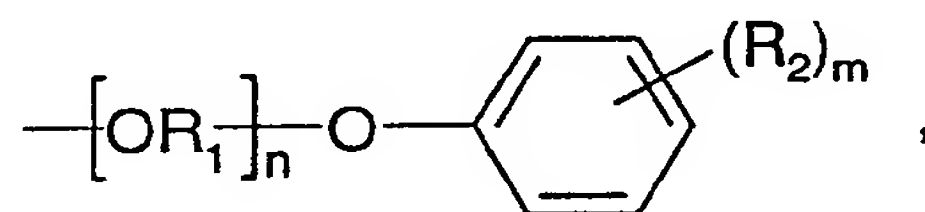
A feature of the invention is where  $n$  is 4 to 25, preferably 16. Another aspect of the invention is wherein the surfactant system component (b) is an alkoxyated sulfonated kraft lignin, preferably an ethoxylated sulfonated kraft lignin. A feature of the invention is wherein the surfactant system component (b) is the sodium salt of an ethoxylated sulfonated kraft lignin having an EO equal to 2 to 4, preferably 3.

Another aspect of the invention is the product obtained by the process of combining the components:

a) at least one alkoxyated polyarylphenol phosphate ester of the formula (1):



wherein  $R_1$  independently is a straight chain or branched  $C_2$ - $C_4$  alkylene,  $R_2$  is phenyl, aryl or alkylaryl, wherein the phenyl nucleus in  $R_2$  is unsubstituted or substituted by one to three groups selected from the group consisting of  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  alkoxy, and  $R_3$  and  $R_4$  are independently selected from the group consisting of hydrogen, sodium, potassium, and



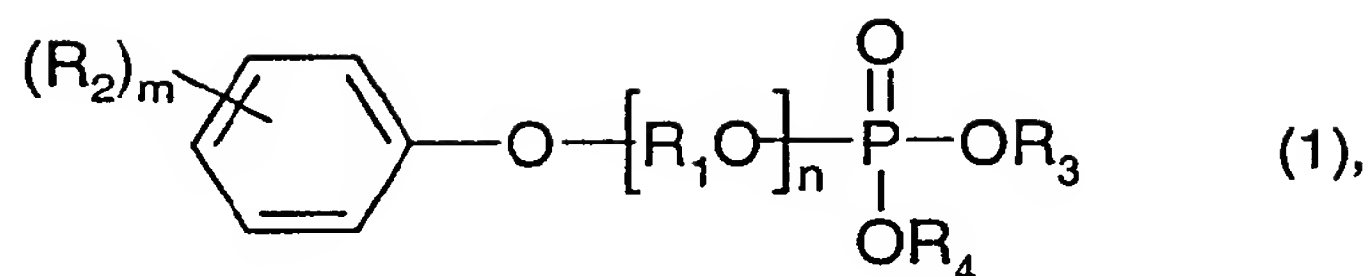
$m$ , is 2 or 3, and  $n$  is a number from 1 to 150 inclusive, and

b) at least one alkoxyated lignosulfonate salt.

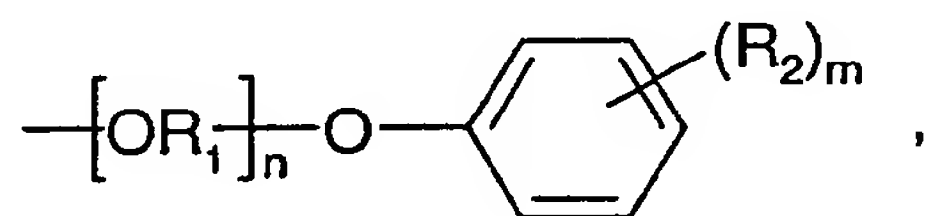
Another aspect of the invention is a chemically integrated surfactant composition comprising:

a) at least one alkoxyated polyarylphenol phosphate ester of the formula (1):

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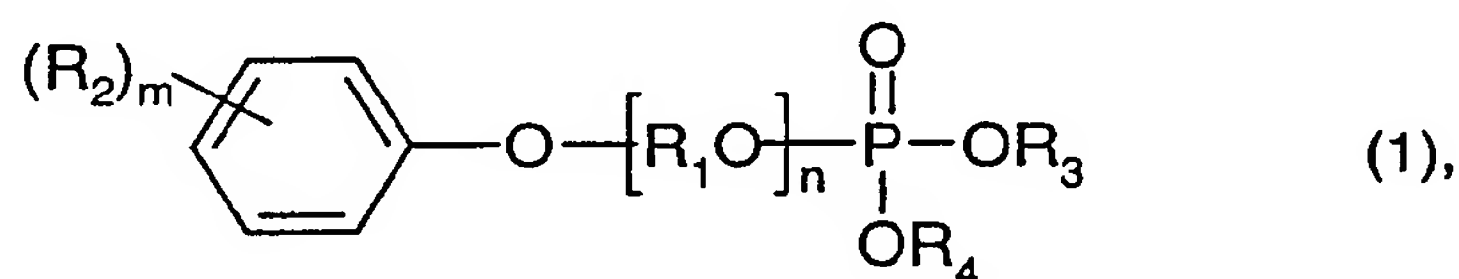
wherein  $R_1$  independently is a straight chain or branched  $C_2$ - $C_4$  alkylene,  $R_2$  is phenyl, aryl or alkylaryl, wherein the phenyl nucleus in  $R_2$  is unsubstituted or substituted by one to three groups selected from the group consisting of  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  alkoxy, and  $R_3$  and  $R_4$  are independently selected from the group consisting of hydrogen, sodium, potassium, and



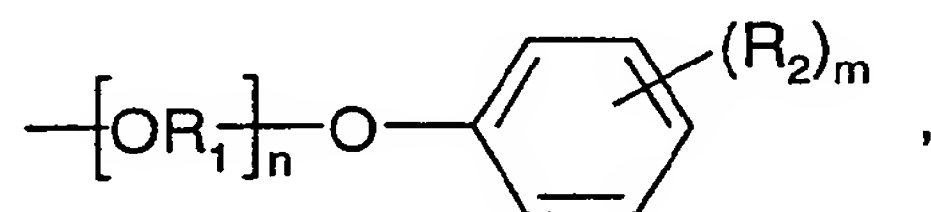
$m$ , is 2 or 3, and  $n$  is a number from 1 to 150 inclusive, and at least one alkoxylated lignosulfonate salt.

Another aspect of the invention is the pesticide formulation comprising at least one pesticide and

a) at least one alkoxylated polyarylphenol phosphate ester of the formula (1):



wherein  $R_1$  independently is a straight chain or branched  $C_2$ - $C_4$  alkylene,  $R_2$  is phenyl, aryl or alkylaryl, wherein the phenyl nucleus in  $R_2$  is unsubstituted or substituted by one to three groups selected from the group consisting of  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  alkoxy, and  $R_3$  and  $R_4$  are independently selected from the group consisting of hydrogen, sodium, potassium, and

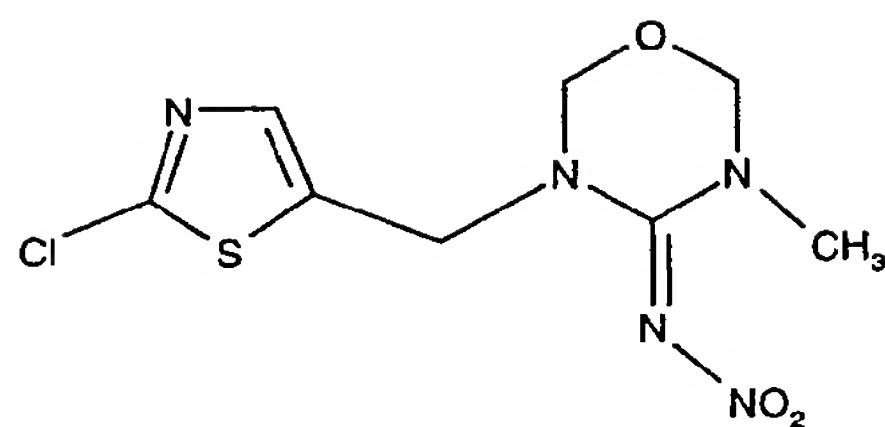


$m$ , is 2 or 3, and  $n$  is a number from 1 to 150 inclusive, and b) at least one alkoxylated lignosulfonate salt.

A preferred embodiment of the invention is the pesticide formulation wherein the pesticide is compound A having the formula:



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Another feature of the invention is the method of protecting crops comprising the step of applying to the locus of the crops in need of protection an agriculturally effective amount of the one or more of the compositions disclosed herein.

The scope of the invention disclosed herein should not be construed to be limited by any particular chemical theory relating to the complexation, equilibration, reaction or acid-base chemistry of the components used to make the surfactants or other ingredients used to make other ultimately useful formulations (e.g. pesticide formulations). In this regard, another aspect of the invention is the surfactant system comprising one or more alkoxyated polyarylphenol phosphate esters (or salts or acid forms thereof) and one or more alkoxyated lignosulfonate salts wherein the constituent components may or may not have interacted chemically so as to result in a change in form of the components. The invention encompasses the static composition of the appropriate components admixed together as well as the chemically integrated surfactant system composition comprising at least one alkoxyated polyarylphenol phosphate ester and at least one alkoxyated lignosulfonate. "Static composition" denotes the composition composed of components wherein the components have not substantially changed by virtue of their combination with other composition components. "Chemically integrated composition" means a composition that results from the natural equilibration, complexation, dissociation or other chemical transformation if any that may occur after combination of the components and prior to ultimate use of the surfactant system in a pesticide formulation. Therefore, the "chemically integrated composition" of the instant invention by definition encompasses the situation where there is a "static composition" as well as any resultant composition occurring at any point in time between initial creation and ultimate use in the field of products containing the surfactant system. In other words, the disclosed invention is not limited to a static composition of chemically unaltered constituent components.

The invention also includes the method of using the surfactant system as a substitute for known APE surfactants.

Another aspect of the invention is the composition comprising the formulation of the surfactant system disclosed above in pesticide formulations that contain one or more other

active ingredients. However, the invention is not limited to pesticide formulations. Other useful formulations that may contain the instantly disclosed surfactant system include shampoo formulations, detergent formulations generally and soap formulations used in the mining industry. The surfactant system presently disclosed is considered to have general applicability as a substitute for known APE surfactants, and therefore would be expected to be useful in many other known formulations. The invention encompasses any formulation obtained by otherwise substituting the instantly disclosed surfactant system for known APEs. The instantly disclosed invention also encompasses any formulation obtained by supplementing compositions containing APEs. Generally, any formulation that conventionally makes use of surfactant additives would be subject to modification by substitution or supplementation with the instantly disclosed surfactant system. Although the surfactant combination herein is disclosed as a surfactant system, it is expected that it will also have other nonsurfactant properties that may be useful independently of any inherent surfactant properties. Depending on the application of the instant invention, it may result in increased bioefficacy and/or reduced toxicity and irritation.

Another aspect of the invention is the composition comprising the formulation of the surfactant system disclosed above in formulations that contain one or more herbicides and one or more safeners (antidotes). When applying herbicides, the cultivated plants may also suffer severe damage owing to factors that include the concentration of the herbicide and the mode of application, the cultivated plant itself, the nature of the soil, and the climatic conditions such as exposure.

The alkoxyated polyarylphenol phosphate esters are either commercially available, prepared by known procedures or otherwise obtained using known chemistry. For example ethoxyated tristyrylphenol phosphate esters may be prepared from the corresponding tristyrylphenol ethoxylate by reaction with phosphorus pentoxide dissolved in phosphoric acid. The tristyrylphenol ethoxylate in turn may be prepared by treating tristyrylphenol with a base (e.g. sodium hydroxide or potassium hydroxide) followed by addition of the desired equivalents of ethylene oxide. Tristyrylphenol is either commercially available, may be prepared by known procedures or otherwise may be prepared using conventional chemistry knowledge. Also mixtures of different phenols (e.g. mixtures of tristyrylphenol and distyrylphenol) may be used as starting materials for preparing the phosphate ester surfactant components of the instant invention.

The alkoxyated lignosulfonates are either commercially available, prepared by known procedures or otherwise obtained using known chemistry. For example, the alkoxyated



lignosulfonates may be obtained by alkoxylation of the lignosulfonates using known alkylene oxide reagents, such as ethylene oxide. In particular, the desirable alkoxyated lignosulfonates are those selected from the group consisting of ethoxylated lignosulfonates, propoxylated lignosulfonates and butoxylated lignosulfonates. Other useful alkoxyated lignosulfonates are those compounds resulting from for example mixed alkoxylation whereby the alkylene oxide units introduced vary or alternate for example between ethylene oxide and propylene oxide. The degree of alkoxylation may vary depending on the desired formulation design parameters, e.g. emulsion stability of pesticide formulations.

The lignosulfonates or sulfonated lignins used to make the alkoxyated lignosulfonates are well known in the art, and are for example derived from the sulfite pulping of wood and by sulfonation of lignins derived from the kraft pulping of wood. The lignin materials used are typically in the salt form (i.e. sodium, potassium, etc.). The lignosulfonates which may be utilized for preparing the alkoxyated lignosulfonate surfactants of the instant invention are commercially available, may be obtained from known procedures or otherwise prepared using known chemistry. Typically lignosulfonates may be obtained by sulfonation of spent sulfite liquors from wood conversion. It is preferable to use purified lignosulfonate material in which the sugars and other polysaccharide constituents have been removed and/or destroyed, or additionally inorganic constituents have been partially or fully eliminated.

The alkoxyated lignosulfonates used to make the surfactant system of the invention are preferably those compounds that are readily available and inexpensive. However, cost of materials is only one factor in selecting the alkoxyated lignosulfonates starting materials. After performing a routine cost-benefit analysis and in view of other design parameters it may become apparent that more expensive and less readily available starting materials may be preferred.

Typically the degree of alkoxylation in the alkoxyated polyarylphenol phosphate ester and in the alkoxyated lignosulfonate is independently measured in terms of the average number of alkylene oxide units therein. The "average number of ethylene oxide units" is designated as an "EO" number. Similarly, the average number of propylene oxide and butylene oxide units is designated as a "PO" and "BO" number, respectively. "Average" is defined as the arithmetic mean of a set of real numbers. A preferred feature of the invention is where there is a continuous and symmetrical bell curve population distribution around the EO, PO or BO number. The alkoxyated surfactant components of the invention may contain mixtures of different alkoxy units, e.g. EO + PO + BO. It is also desirable that

there be low dispersion preferably within one standard deviation ( $\sigma$ ) of the mean (average EO).

**Table:** Degree of alkoxylation in the surfactant system components.

	Alkoxylated polyarylphenol phosphate ester			Alkoxylated lignosulfonate		
	EO	PO	BO	EO	PO	BO
<b>Preferably</b>	1 to 150	1 to 100	1 to 50	1 to 12	1 to 6	1 to 3
<b>More preferably</b>	4 to 25	2 to 20	1 to 10	1 to 4	1 to 3	1 to 2
<b>Most preferably</b>	16	8	4	3	2	1

By “alkyl” is meant an alkyl group that may be linear or branched. By “aryl” is meant either a non-heteroaromatic ring system or heteroaromatic ring system. By “alkylaryl” is meant an aryl group substituted by one or more alkyl groups, wherein the “aryl” may be either a non-heteroaromatic ring system or heteroaromatic ring system.

By “kraft lignin” is meant material typically recovered from alkaline pulping black liquors such as are produced in the kraft, soda and other well known alkaline pulping operations.

By “sulfonated lignin” is meant the product which is obtained by the introduction of sulfonic acid groups into the kraft lignin molecule, as may be accomplished by reaction of the kraft lignin with sulfite or bisulfite compounds, so that the kraft lignin is rendered soluble in water.

By “sulfite lignin” is meant the reaction product of lignin which is obtained during the sulfite pulping of wood, and is a principle constituent of spent sulfite liquor.

By “alkoxylated lignosulfonate” is meant the reaction product obtained by alkoxyating lignosulfonates with an alkylene oxide, such as ethylene oxide.

Another preferred feature of the present invention is the combination of the presently disclosed surfactant system with one or more co-surfactants. The co-surfactants are those compounds known in the art for formulating surfactant systems. The co-surfactants include

polyglycol ethers, aliphatic alcohols, cycloaliphatic alcohols, alkylphenols (e.g. nonylphenol), saturated fatty acids, unsaturated fatty acids, polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, or saturated or unsaturated fatty acids. Said derivatives contain 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon moiety. A more preferred co-surfactant is a nonionic co-surfactant, especially the nonionic co-surfactant selected from the group consisting of ethylene glycol and polyethylene glycol. Other preferred surfactants may include, castor oil ethoxylates, tristerylphenol ethoxylates, ethylene oxide/propylene oxide block copolymers (pluronics), and/or ethylene oxide/propylene oxide block copolymers of aliphatic alcohols.

A preferred aspect of the invention includes the combination of the surfactant system herein with a liquid pesticide composition so as to obtain an emulsifiable concentrate formulation which can be directly mixed with water or other aqueous solution to give an aqueous pesticide formulation without special mixing procedures.

A preferred aspect of the invention includes the combination of the surfactant system herein with a solid pesticide composition so as to obtain a suspension concentrate formulation which can be directly mixed with water or other aqueous solution to give an aqueous pesticide formulation without special mixing procedures.

A preferred aspect of the invention includes the combination of the surfactant system herein with a liquid pesticide composition and solid pesticide composition so as to obtain a suspoemulsion concentrate formulation which can be directly mixed with water or other aqueous solution to give an aqueous pesticide formulation without special mixing procedures.

The following examples illustrate further some of the specific features of the invention but are not intended to limit its scope. Where not otherwise specified throughout this specification and claims, temperatures are given in degrees centigrade.

One preferred feature of the invention includes combining the surfactant system previously described with a liquid active ingredient to obtain an emulsifiable concentrate formulation which can be readily diluted with water or other liquid carriers requiring no special handling or mixing procedures. An example of such a formulation follows:

### Example 1

An aqueous emulsion concentrate containing Compound A as active ingredient was prepared according to the following formulation (indicated percentages are weight percentages):

- 47.6% Compound A (see Table),
- 4.0% tristyrylphenol ethoxylate phosphate ester (16EO),
- 2.0% ethoxylated lignosulfonate (3EO),
- 5.0% glycerin,
- 0.1% xanthan gum,
- 0.1% silicone antifoam,
- 0.05% preservative,
- 2.0% attapulgite clay, and water to make up 100%.

The above ingredients were formulated as follows: (1) A premix of water, the Compound A, the ethoxylated tristyrylphenol and the ethoxylated lignosulfonate is prepared. (2) The premix from (1) is ground to a fine particle size. (3) The remaining ingredients are added to the premix followed by mixing until uniform composition is obtained.

### Example 2

An aqueous emulsion concentrate containing Compound A, mefenoxam, fludioxinil and difenoconazole as active ingredient was prepared according to the following formulation (indicated percentages are weight percentages):

- 20.6% Compound A (see Table 3),
- 0.35% mefenoxam,
- 0.25% fludioxinil,
- 1.3% difenoconazole,
- 4.0% tristyrylphenol ethoxylate phosphate ester (16EO),
- 2.0% ethoxylated lignosulfonate (3EO),
- 0.1% sodium hydroxide (50% aqueous solution)
- 0.1% nonylphenol,
- 20.0% glycerin,
- 10.0% titanium oxide,

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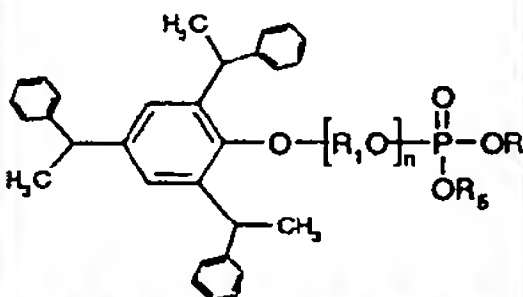
2.5% blue pigment,  
0.75% montmorillonite clay,  
0.13% xanthan gum,  
0.06% preservative, and water to make up 100%.

The above ingredients were formulated as follows: (1) A premix of water, the Compound A, the mefenoxam, the fludioxinil, the difenoconazole, the ethoxylated tristyrylphenol and the ethoxylated lignosulfonate is prepared. (2) The premix from (1) is ground to a fine particle size. (3) The remaining ingredients are added to the premix followed by mixing until uniform composition is obtained.

The crop protection compositions which are part of the instantly disclosed invention may be formulated in a form suitable for the intended application. Types of formulations include for example a flowable (FL) flowable concentrate for seed treatment (FS), wettable powder (WP), wettable dispersible granules (WDG), oil miscible flowable concentrate (OF), suspension concentrate (SC), emulsifiable concentrate (EC), liquid (L), water in oil emulsions (EW), granules (GR) water dispersible powder for slurry treatment (WS) and dry flowable (DF).

Some additional preferred embodiments of the instant invention are contained in Tables 1 and 2 below.

**Table 1:** Crop protection formulations containing surfactant, specified co-surfactant components and one or more active technical components.

	Alkoxyated polyarylphenol phosphate ester		Alkoxyated lignosulfonate salt		Co-surfactant	Active Technical	Active Technical	Active Technical
								
	(Component A)		(Component B)					
	R <sub>1</sub>	n	Salt	Degree of alkoxylation				
				n		T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>
1	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	metolachlor*		
2	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	3	Butoxy EO/PO block polymer	metolachlor*		
3	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	EO/PO block polymer	atrazine		
4	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	ethylene glycol	atrazine		
5	-CH <sub>2</sub> CH <sub>2</sub> -	4 to 25	Na	2 to 4	EO/PO block polymer	atrazine		
6	-CH <sub>2</sub> CH <sub>2</sub> -	4 to 25	Na	3	EO/PO block polymer	atrazine		
7	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2	EO/PO block polymer	atrazine		
8	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Castor oil ethoxylate	atrazine	metolachlor*	
9	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	atrazine	metolachlor*	
10	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Castor oil ethoxylate	flumetralin		
11	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Castor oil ethoxylate	oxasulfuron		
12	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	tristyrylphenol ethoxylate	propiconazole		



13	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	metribuzin	metolachlor*	
14	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	3	Butoxy EO/PO block polymer	metribuzin	metolachlor*	
15	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	flumetsulam	metolachlor*	
18	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	3	Butoxy EO/PO block polymer	flumetsulam	metolachlor*	
17	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Castor oil ethoxylate	flumetsulam	metolachlor*	atrazine
18	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	flumetsulam	metolachlor*	atrazine
19	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	mefenoxam		
20	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	mefenoxam	fludioxinil	
21	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	metalaxyl		
22	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	metalaxyl	fludioxinil	
23	-CH <sub>2</sub> CH <sub>2</sub> -	4 to 25	Na	2 to 4	Butoxy EO/PO block polymer	diazinon		
24	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	diazinon		
25	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	dicamba		
26	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Castor oil ethoxylate	dicamba		
27	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	nonylphenol	COMPOUN D A		
28	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	nonylphenol	COMPOUN D A	mefenoxam	
29	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	nonylphenol	COMPOUN D A	mefenoxam	fludioxinil
30	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	nonylphenol	COMPOUN D A	difenoconazole	mefenoxam + fludioxinil
31	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	nonylphenol	COMPOUN D A	difenoconazole	
32	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	nonylphenol	COMPOUN D A	fludioxinil	
33	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Castor oil ethoxylate	COMPOUN D A		
34	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glyphosate or salts		

35	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glyphosate isopropylam monium		
36	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glyphosate sesquisodiu m		
37	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glyphosate trimesium		
38	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	fluthiacet- methyl		
39	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glyphosate or salts	fluthiacet- methyl	
40	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glyphosate isopropylam monium	fluthiacet- methyl	
41	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glyphosate sesquisodiu m	fluthiacet- methyl	
42	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glyphosate trimesium	fluthiacet- methyl	
43	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	flumiclorac- pentyl		
44	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glyphosate or salts	flumiclorac- pentyl	
45	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glyphosate isopropylam monium	flumiclorac- pentyl	
46	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glyphosate sesquisodiu m	flumiclorac- pentyl	
47	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glyphosate trimesium	flumiclorac- pentyl	
48	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glufosinate or salts		
49	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glufosinate		
50	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glufosinate ammonium		
51	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glufosinate or salts	fluthiacet- methyl	
52	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glufosinate	fluthiacet- methyl	
53	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glufosinate ammonium	fluthiacet- methyl	

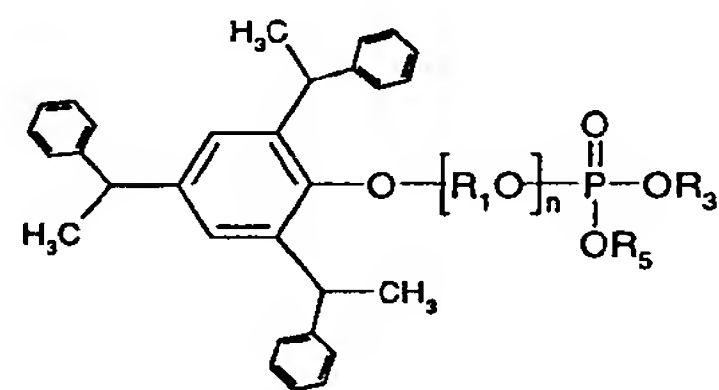
<b>54</b>	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glufosinate or salts	flumiclorac- pentyl	
<b>55</b>	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glufosinate	flumiclorac- pentyl	
<b>56</b>	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glufosinate ammonium	flumiclorac- pentyl	
<b>57</b>	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glyphosate	atrazine	
<b>58</b>	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glyphosate	metolachlor*	atrazine
<b>59</b>	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glyphosate salt	atrazine	
<b>60</b>	-CH <sub>2</sub> CH <sub>2</sub> -	16	Na	2 to 4	Butoxy EO/PO block polymer	glyphosate salt	metolachlor*	atrazine

\* includes the racemic mixtures or s-metolachlor

Degree of alkoxylation = average number of alkylene oxide units

**Table 2. Crop protection formulations:**

Surfactant system used:



plus Ethoxylated Kraft Lignosulfonate Salt

R<sub>1</sub>, R<sub>3</sub>, R<sub>5</sub> and n are defined above

Active technical ingredients used and formulation type:

ACTIVE TECHNICAL	ACTIVE TECHNICAL	ACTIVE TECHNICAL	FORMULATION TYPE
T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>	
Atrazine			FL, WP, WDG, OF
Atrazine	Flumetsulam		FL, WP, WDG, OF
Atrazine	Metolachlor		SC, OF, WDG
Atrazine	Flumetsulam	Metolachlor	SC, OF, WDG
Ametryn			OF, EC, WP, L, WDG
Chlorothalonil			FL, WDG, WP
Chlorothalonil	Metalaxyl		EC, WDG, WP, OF
Cyprodinil			EC, WP, OF, WDG
Cyromazine			WP, L
Diazinon			EW, W, EC, WDG
Dicamba			GR, L
Dicamba	Prosulfuron		WDG
Difenoconazole			WP, EC, WS, FS
Difenoconazole	Metalaxyl		WP, EC, WS, FS

Diofenolan			EC, WP
Fenoxycarb			WP, WDG, EC
Fenoxycarb	Pymetrozine		WP, WDG, EC
Fludioxinil			L, FS, WDG, WP
Fludioxinil	Mefenoxam		L, FS, WDG, WP
Fludioxinil	Metalaxyl		L, FS, WDG, WP
Fludioxinil	Propiconazole		L, FS, WDG, WP
Flumetralin			EC, WDG, WP
Flumetralin	Oxasulfuron		EC, WDG, WP
Flumetsulam			EC, WDG, WP, OF
Flumetsulam	Metolachlor		EC, WDG, WP, OF
Fluometuron			L, DF, WP
Fluthiacet-methyl			EC, WDG, WP
Fluthiacet-methyl	Glyphosate		EC, WDG, WP
Fluthiacet-methyl	Oxasulfuron		EC, WDG, WP
Isazofos			EC, GR
Mancozeb			SC, FL, WDG, WP
Mancozeb	Metalaxyl		SC, FL, WDG, WP
Mefenoxam			EC, WP, GR, FL, L
Metalaxyl			EC, GR, L, WP
Methidathion			EC, WP
Metolachlor			EC, DF, GR
Metolachlor	Metribuzin		WDG, OF, EC
Metolachlor	Simazine		WDG, OF, SC
s-Metolachlor			EC, DF, GR
s-Metolachlor	Metribuzin		WDG, OF, EC
s-Metolachlor	Simazine		WDG, OF, SC
Metribuzin			EC, DF, WDG, OF
Norflurazon			DF, GR
Primisulfuron			WDG, WP
Primisulfuron	Prosulfuron		WDG, WP
Profenofos			EC

Prometon			EC, FL, OF, WP
Prometryn			WP, L, OF
Propiconazole			EC, WP
Pymetrozine			WDG, WP
Simazine			WP, WDG, L, GR
Triforine			WP, EC
Trinexapac-ethyl			EC, WDG,
COMPOUND A			WDG, OF, EC, SC
COMPOUND A	Difenoconazole		WDG, OF, EC, SC
COMPOUND A	Fludioxinil		WDG, OF, EC, SC
COMPOUND A	Difenoconazole	Fludioxinil	WDG, OF, EC, SC
COMPOUND A	Mefenoxam		WDG, OF, EC, SC
COMPOUND A	Difenoconazole	Mefenoxam	WDG, OF, EC, SC
COMPOUND A	Fludioxinil	Mefenoxam	WDG, OF, EC, SC
COMPOUND A	Difenoconazole	Fludioxinil plus Mefenoxam	WDG, OF, EC, SC
COMPOUND B			WDG, WP
COMPOUND C			WDG, WP, EC
COMPOUND D			EC, WP, WDG

EO = average number of ethylene oxide units

<u>Code</u>	<u>Description of formulation code</u>
DF	dry flowable
EC	emulsifiable concentrate
EW	water in oil emulsions
FL	flowable
FS	flowable concentrate for seed treatment
GR	granules
L	liquid
OF	oil miscible flowable concentrate
SC	suspension concentrate (suspoemulsion)
WDG	wettable dispersible granules
WP	wettable powder
WS	water dispersible powder for slurry treatment



**Table 3: Structures for Compounds A to D:**

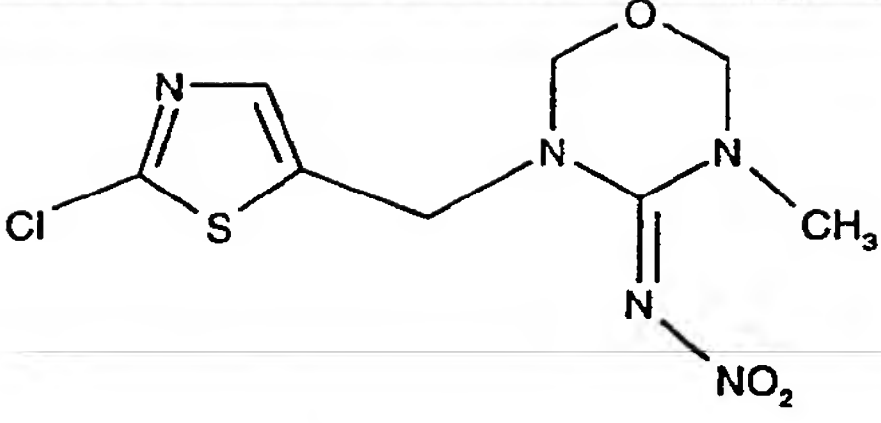
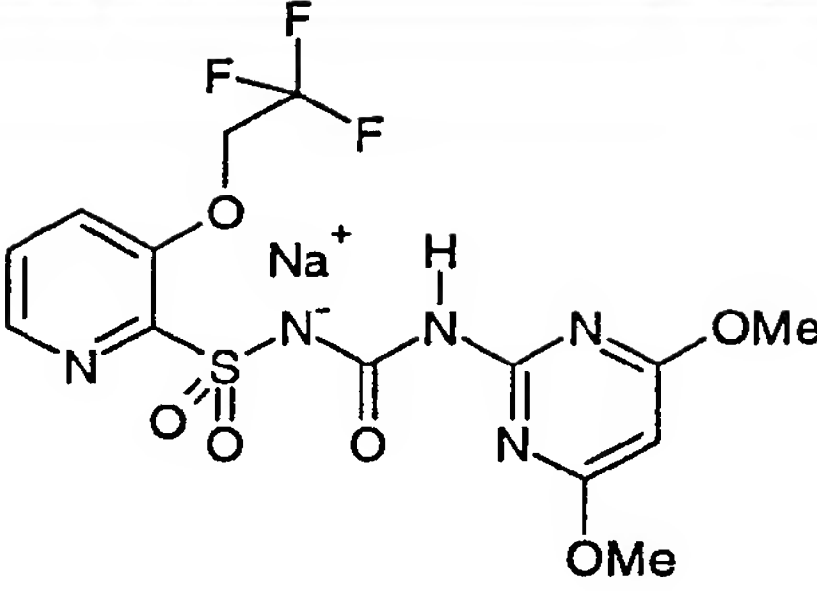
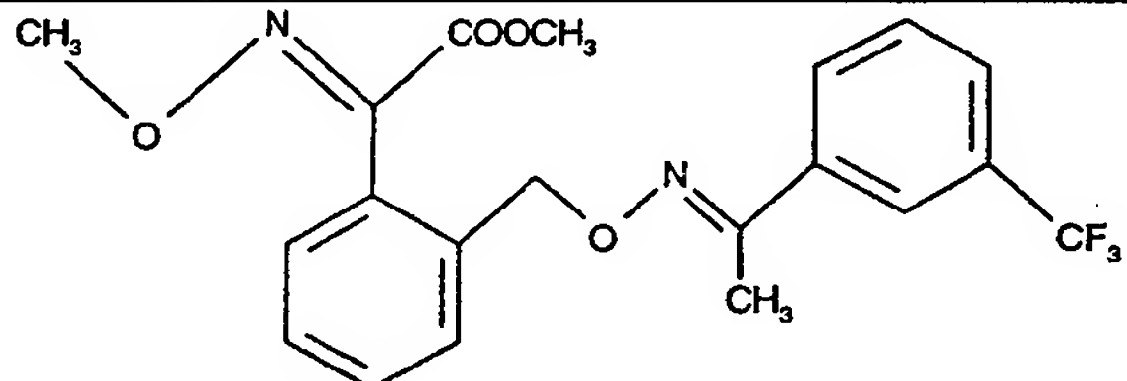
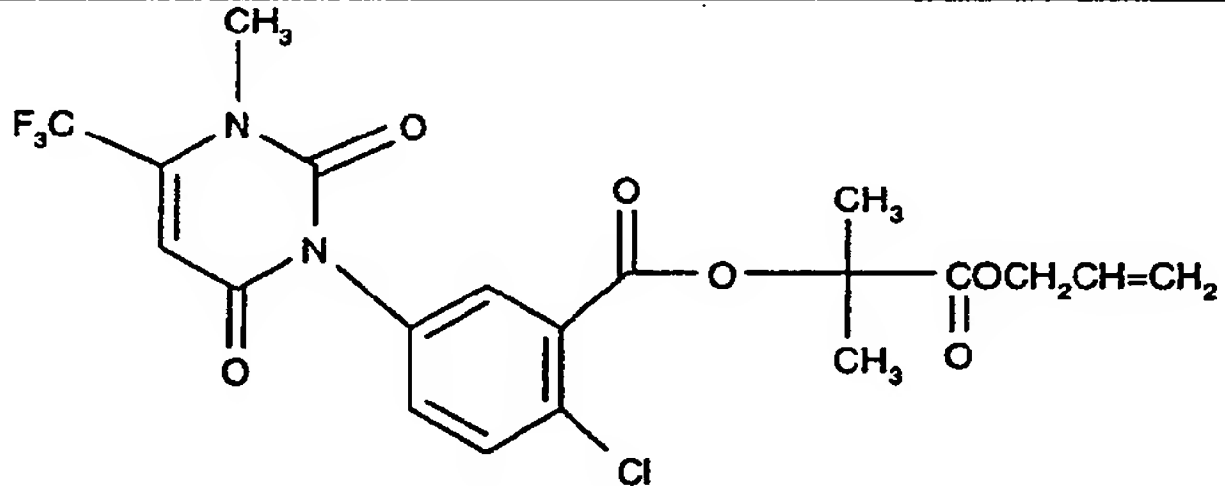
	Structure
COMPOUND A	
COMPOUND B	
COMPOUND C	
COMPOUND D	

Table 4 lists some examples of useful components that may be used to formulate the compositions of the instant invention. However, the invention is not limited to the use of the indicated components in the table. Table 5 provides some sources for commercially available materials. Nevertheless, one of ordinary skill would realized that many of the materials that could be used to practice the instantly disclosed invention may be obtained from any suitable source.

**Table 4: Examples of components that may be used to formulate the compositions of the instant invention.**

<b>Product Name</b>	<b>Supplier</b>	<b>Description</b>
Aromatic 150	Exxon Corporation	aromatic hydrocarbon solvent
Pegasol R-150	Mobil Chemical Company	aromatic hydrocarbon solvent
Cyclo Sol 150	Shell Chemical Company	aromatic hydrocarbon solvent
Pluronic P-65	BASF Corporation	EO-PO block copolymer
Toximul 8323	Stepan Company	EO-PO block copolymer
Antifoam A	Dow Corning Corporation	silicone antifoaming agent
Y-6067	Osi Specialties, Inc.	silicone antifoaming agent
Proxel GXL	Zeneca Inc.	biostatic
Nipacide BIT20	Nipa Hardwicke, Inc.	biostatic
Renex 36	ICI Surfactants	Tridecyl alcohol (6EO)
Rhodasurf BC-610	Rhodia Inc.	Tridecyl alcohol (6EO)
Genopol X-060	Clariant Corporation formerly Hoechst Celanese Corporation	Tridecyl alcohol (6EO)
Witconol TD-60	Witco Corporation	Tridecyl alcohol (6EO)
Rhodopol 23	Rhodia Inc.	Xanthan gum
Kelzan	Zeneca Inc.	Xanthan gum

**Table 5: Names and address of suppliers of materials.**

<b>Supplier</b>	<b>Address</b>
Witco Corporation	5777 Frantz Road, P.O. Box 646, Dublin, Ohio 43017
Stepan Company	Northfield, Illinois 60093
Dow Corning Corporation	Midland, MI 48686
Zeneca Inc.	Wilmington, DE 19897
BASF, Corporation	Mt. Olive, NJ 07828
Rhodia, Inc.	Cranbury, NJ 08512
Nipa Hardwicke, Inc.	3411 Silverside Road, 104 Hagley Bldg., Wilmington, DE 19810
Osi Specialities, Inc.	Greenwich, CT 06831
ICI Surfactants	Wilmington, DE 19850
Clariant Corporation	Charlotte, NC 28201
Shell Chemical Company	Houston, TX 77251
Exxon Corporation	Houston, TX 77001
Mobil Chemical Company	Houston, TX 77032

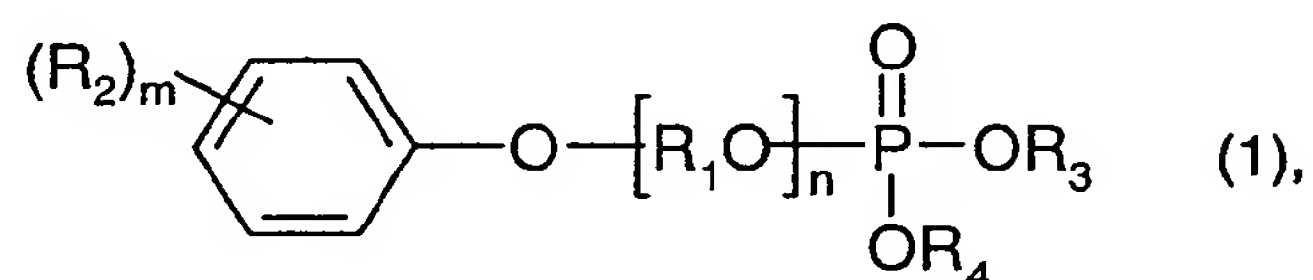
In summary, it is seen that this invention provides new salt compounds useful as surfactants. In particular, the surfactants of the instant invention are useful for formulating agrochemical compositions. Variations may be made in proportions, procedures and materials without departing from the scope of the invention as defined by the following claims.

## CLAIMS

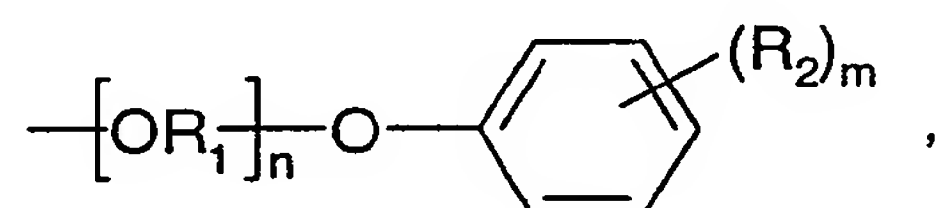
WHAT IS CLAIMED IS:

1. A surfactant system comprising:

a) at least one alkoxyated polyarylphenol phosphate ester of the formula (1):



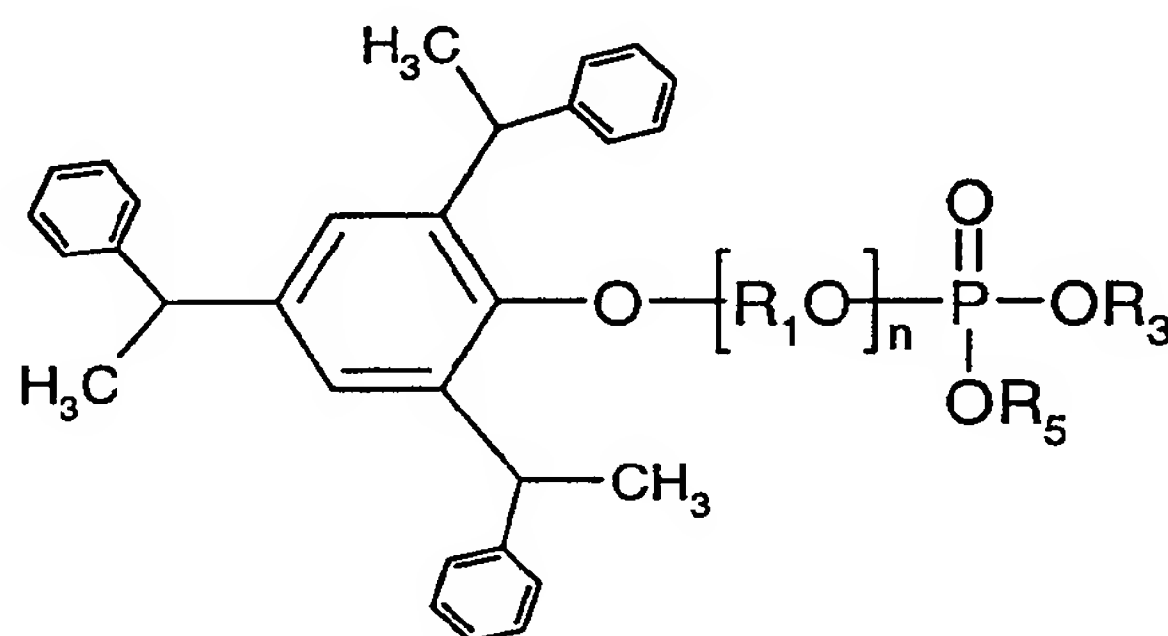
wherein  $R_1$  independently is a straight chain or branched  $C_2$ - $C_4$  alkylene,  $R_2$  is phenyl, aryl or alkylaryl, wherein the phenyl nucleus in  $R_2$  is unsubstituted or substituted by one to three groups selected from the group consisting of  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  alkoxy, and  $R_3$  and  $R_4$  are independently selected from the group consisting of hydrogen, sodium, potassium, and



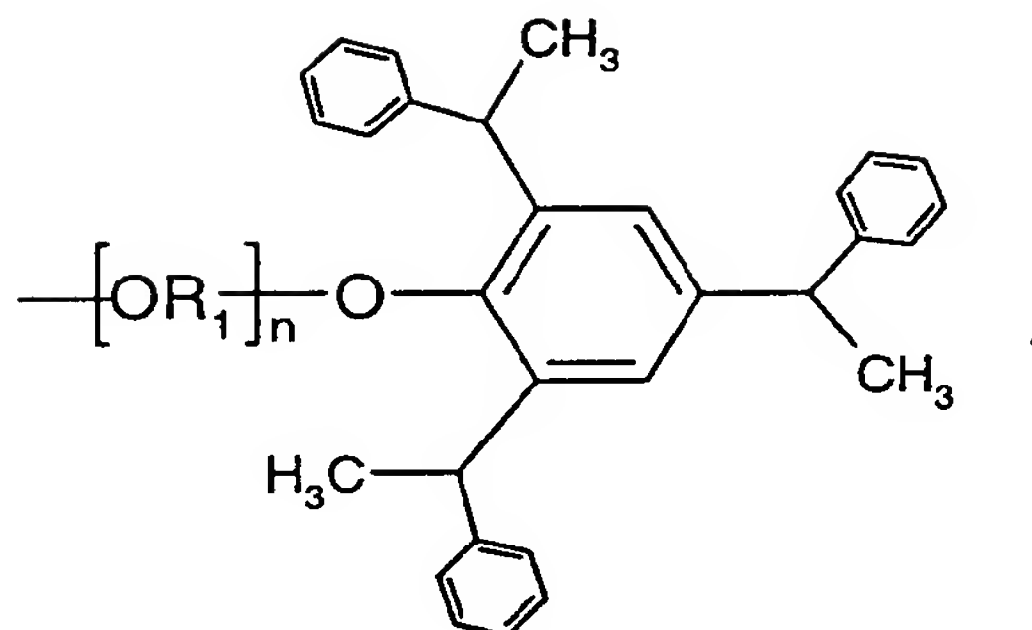
$m$ , is 2 or 3, and  $n$  is a number from 1 to 150 inclusive, and

b) at least one alkoxyated lignosulfonate salt.

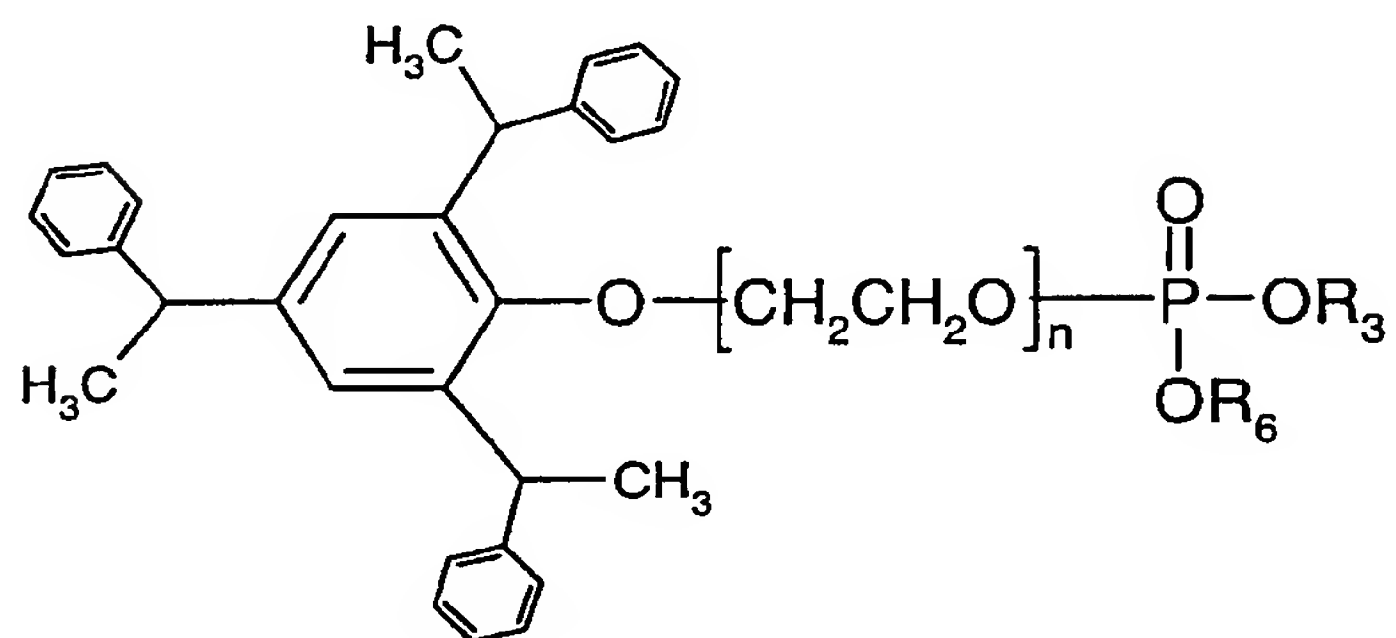
2. A surfactant system of claim 1, wherein component (a) is the phosphate ester having the formula:



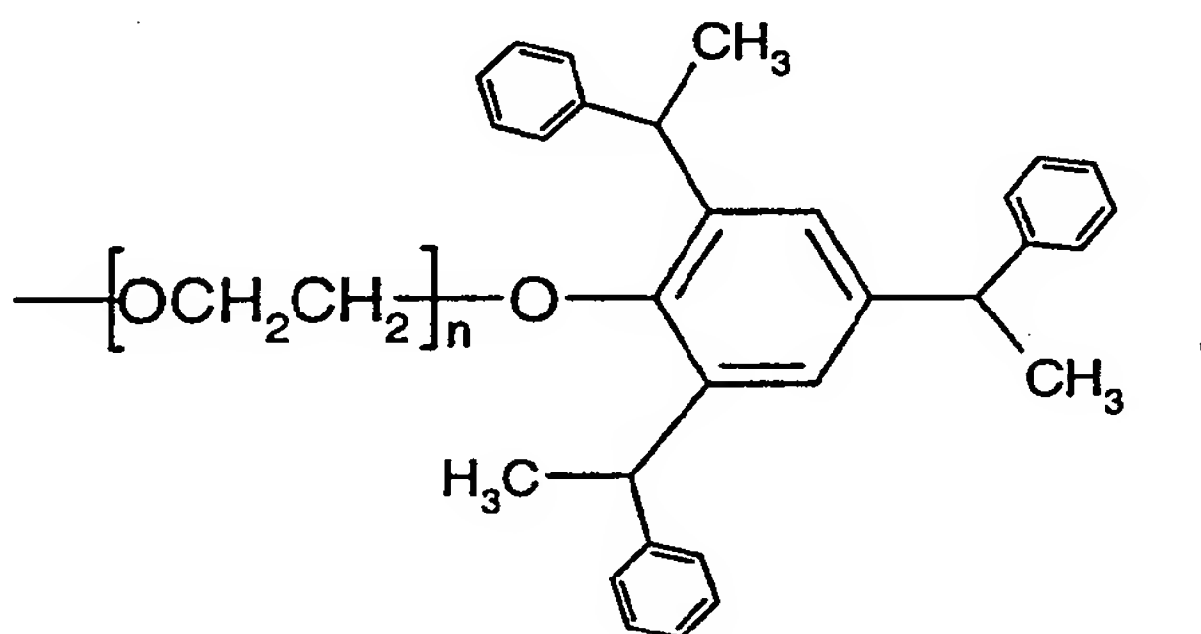
wherein  $R_1$  and  $n$  are defined as above, and  $R_3$  and  $R_5$  are independently selected from the group consisting of hydrogen, sodium, potassium, and



3. A surfactant system of claim 1, wherein component (a) is the phosphate ester having the formula:



wherein  $n$  is defined as above, and  $R_3$  and  $R_6$  are independently selected from the group consisting of hydrogen, sodium, potassium, and



4. A surfactant system according to claim 3, wherein  $n$  is 4 to 25.

5. A surfactant system according to claim 3, wherein  $n$  is 16.

6. A surfactant system according to claim 3, wherein component (b) is an alkoxyated sulfonated kraft lignin.

7. A surfactant system according to claim 4, wherein component (b) is an ethoxylated sulfonated kraft lignin.

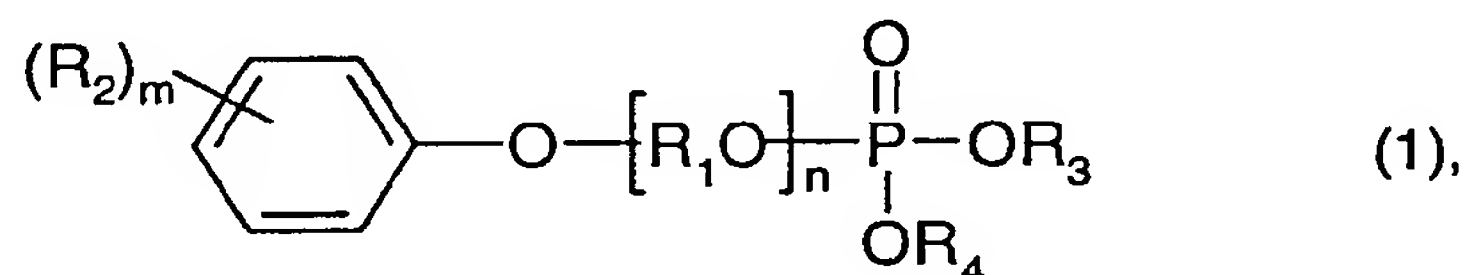
8. A surfactant system according to claim 7, wherein component (b) is the sodium salt of an ethoxylated sulfonated kraft lignin having an EO equal to 2 to 4.

9. A surfactant system according to claim 8, wherein component (b) is the sodium salt of an ethoxylated sulfonated kraft lignin having an EO equal to 3.

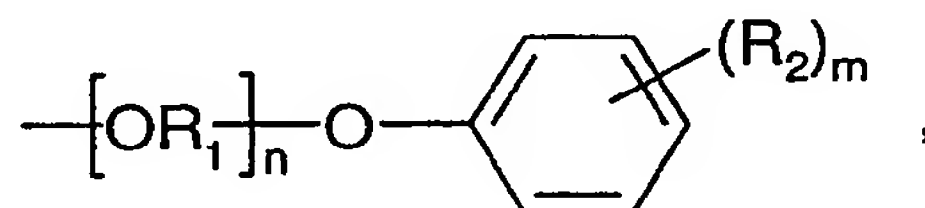
10. A surfactant system according to claim 8, wherein component (a) n is 16.

11. A product obtained by the process of combining the components:

a) at least one alkoxyated polyarylphenol phosphate ester of the formula (1):



wherein  $R_1$  independently is a straight chain or branched  $C_2$ - $C_4$  alkylene,  $R_2$  is phenyl, aryl or alkylaryl, wherein the phenyl nucleus in  $R_2$  is unsubstituted or substituted by one to three groups selected from the group consisting of  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  alkoxy, and  $R_3$  and  $R_4$  are independently selected from the group consisting of hydrogen, sodium, potassium, and



$m$ , is 2 or 3, and  $n$  is a number from 1 to 150 inclusive, and

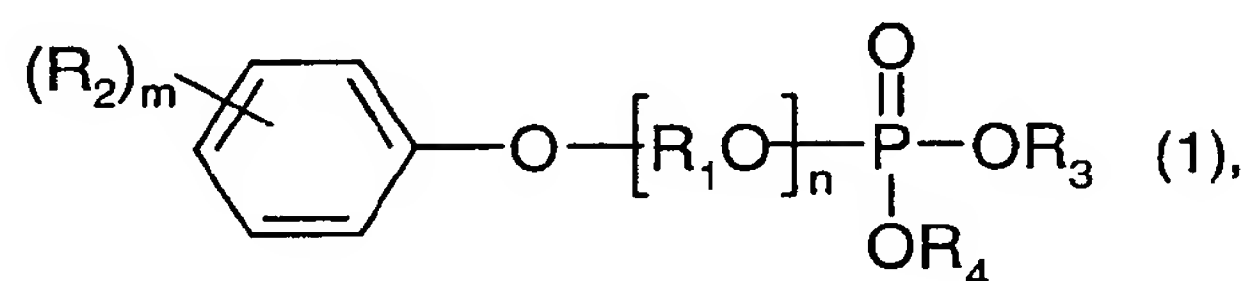
b) at least one alkoxyated lignosulfonate salt.

12. A product according to claim 11, wherein component (a) n is 16 and component (b) has an EO equal to 2 to 4.

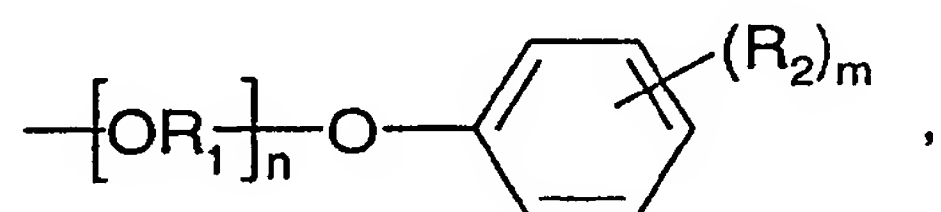
13. A chemically integrated surfactant composition comprising:



a) at least one alkoxyated polyarylphenol phosphate ester of the formula (1):



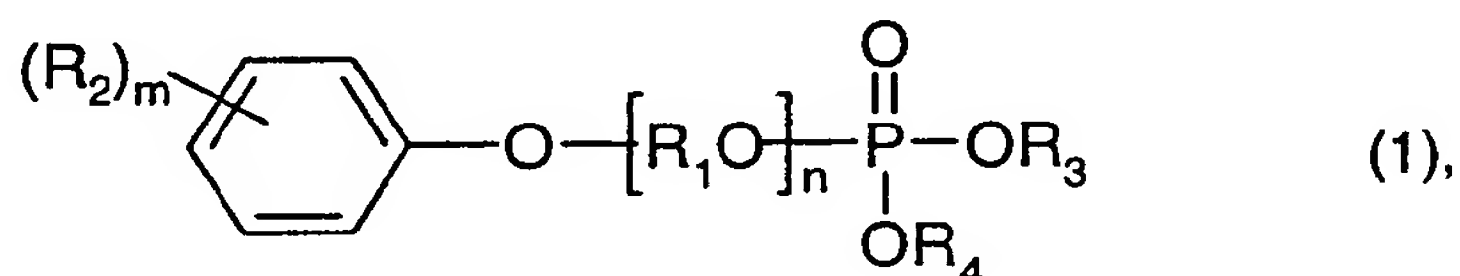
wherein  $R_1$  independently is a straight chain or branched  $C_2$ - $C_4$  alkylene,  $R_2$  is phenyl, aryl or alkylaryl, wherein the phenyl nucleus in  $R_2$  is unsubstituted or substituted by one to three groups selected from the group consisting of  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  alkoxy, and  $R_3$  and  $R_4$  are independently selected from the group consisting of hydrogen, sodium, potassium, and



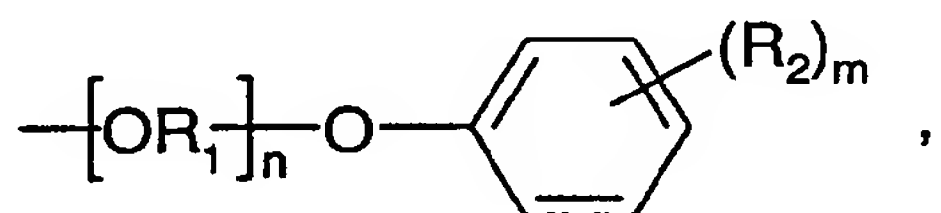
$m$ , is 2 or 3, and  $n$  is a number from 1 to 150 inclusive, and at least one alkoxyated lignosulfonate salt.

14. A pesticide formulation comprising at least one pesticide and

a) at least one alkoxyated polyarylphenol phosphate ester of the formula (1):



wherein  $R_1$  independently is a straight chain or branched  $C_2$ - $C_4$  alkylene,  $R_2$  is phenyl, aryl or alkylaryl, wherein the phenyl nucleus in  $R_2$  is unsubstituted or substituted by one to three groups selected from the group consisting of  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  alkoxy, and  $R_3$  and  $R_4$  are independently selected from the group consisting of hydrogen, sodium, potassium, and

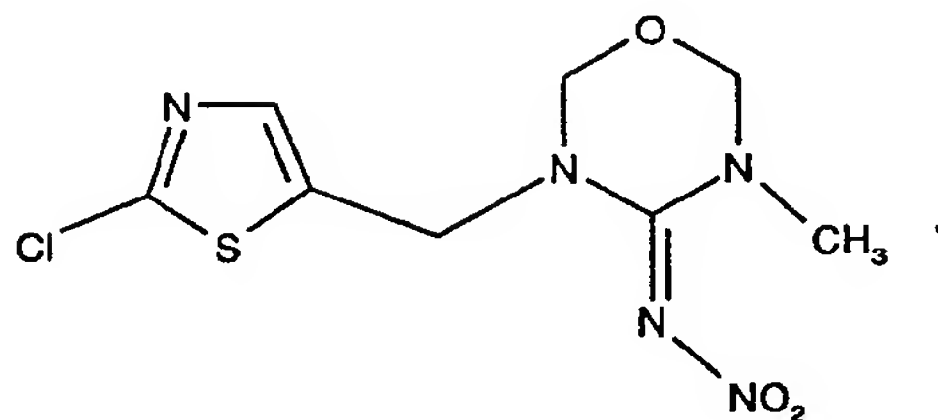


$m$ , is 2 or 3, and  $n$  is a number from 1 to 150 inclusive, and

b) at least one alkoxyated lignosulfonate salt.

- 27 -

15. A pesticide formulation of claim 14 wherein the pesticide is compound A having the formula:



16. A method of protecting crops comprising the step of applying to the locus of the crops in need of protection an agriculturally effective amount of the formulation of claim 14.

17. A method of protecting crops comprising the step of applying to the locus of the crops in need of protection an agriculturally effective amount of the formulation of claim 15.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 00/09134

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 A01N25/30 A01N51/00 C11D1/37

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 A01N C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 224 845 A (HOECHST AG) 10 June 1987 (1987-06-10)  page 3, line 20 -page 4, line 6 page 5, line 21 - line 23 page 5, line 31 - line 33 page 9; example 2 ---	1-6, 11, 13, 14, 16, 17
A	EP 0 190 995 A (CIBA GEIGY AG) 13 August 1986 (1986-08-13) page 3, paragraph 3 -page 4, paragraph 1 page 5, paragraph 3 -page 6, paragraph 1 page 7, paragraph 2 ---	1-17
A	EP 0 257 533 A (HOECHST AG) 2 March 1988 (1988-03-02) page 2, line 8 - line 52 ---	1-17
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \* & \* document member of the same patent family

Date of the actual completion of the international search

31 January 2001

Date of mailing of the international search report

08/02/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Lamers, W

INTERNATIONAL SEARCH REPORT

Ir.      ational Application No
PCT/EP 00/09134

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 257 286 A (HOECHST AG) 2 March 1988 (1988-03-02) column 1, line 29 -column 2, line 21 -----	1-17

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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